

OPTIMIZED CONDITIONS FOR GRAFTING REACTION OF POLY (METHYL METHACRYLATE) ONTO TALC FILLER

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ABSTRACT

In this study, poly(methyl methacrylate) (PMMA) grafted onto talc was produced using free radical polymerization. Hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) were used as a redox initiator/co-catalyst system. Grafting copolymerization was carried out under nitrogen atmosphere since it is known that oxygen presence will terminate the free radical mechanism. The PMMA homopolymer formed during the reaction was removed from the graft copolymer by Soxhlet extraction using acetone. The grafting percentage and grafting efficiency were systematically investigated. The parameter variables; reaction time, reaction temperature and concentration of ammonium ferrous sulfate directly influenced the grafting percentage. The percent grafting increased to a certain value in each variable. The optimum conditions for reaction period, reaction temperature and initiator concentrations were 60 minutes, $52^\circ C$ and 4.87×10^{-3} mol, respectively. Fourier-transform infrared spectroscopy was used to observe the difference between ungrafted with grafted talc. The formation of ester group peak in talc-g-PMMA spectrum has proven that the presence of PMMA onto the talc surface.

Key Words : Graft copolymers, Free radical, Copolymerization

1.0 INTRODUCTION

Fillers describe as those inert, solid materials which are physically dispersed in the polymer matrix, without significantly affecting the molecular structure of the polymer. The term is restricted to those materials which are in the form of discrete particles or of fibers not exceeding a few inches in length [1]. Talc filler is a natural hydrated magnesium silicate with the formula $Mg_3Si_4O_{10}(OH)_2$. It is a very common metamorphic mineral in metamorphic belts which contain ultramafic rocks, such as soapstone (a high-talc rock), and within white schist and blue schist metamorphic terrains. Talc is a metamorphic mineral resulting from the metamorphism of magnesium minerals such as pyroxene, amphibole, olivine and other similar minerals in the presence of carbon dioxide and water. This is known as talc carbonation or steatization and produces a suite of rocks known as talc carbonates. Talc is primarily formed via hydration and carbonation of serpentine[1].

A homogeneous distribution of fillers in the matrix of polymer is important, in order that as many polymer chains as possible can be bound to the free filler surface. Block and graft copolymers rank among the most interesting tailor-made polymer products because they combine the properties of several different homopolymers in a single molecule. Because of the presence of a covalent bond between each segment, these types of copolymers lead to well-organized nanoscale morphologies both in bulk and in solution. Block and graft copolymers are used for a variety of applications, including impact-resistant materials,

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thermoplastic elastomers, compatibilizers, polymeric emulsifiers, membranes, and drug-delivery systems. The possibility of the design of optimal material properties through the use of appropriate graft or block structures suggests tremendous commercial potential, and both block and graft copolymers have achieved considerable industrial importance.

There is still no attempt for graft polymerization of methyl methacrylate (MMA) onto talc filler. Most of the researches are more focused on the mechanical properties of talc filled onto MMA using blending technique or extrusion technique. However, there are several researches about grafting polymerization of MMA onto fibers and fillers. The optimum conditions for the graft copolymerization of methyl methacrylate (MMA) onto palm oil empty fruit bunch fiber (OPEFB) using hydrogen peroxide as an initiator has been reported by Abu Bakar, *et al.* [2]. Other article has reported about grafting MMA onto stone ground wood using $\text{H}_2\text{O}_2\text{-Fe}^{2+}$ method [3]. Therefore, in order to obtain all the optimum conditions for graft copolymerization of methyl methacrylate (MMA) onto talc filler using hydrogen peroxide as initiator, effect of reaction temperature, reaction period and amount of initiator on the grafting were investigated.

2.0 MATERIALS AND METHODS

2.1 Materials

The talc filler in powder form used throughout this study was received from Chung Chemical Sdn. Bhd., Malaysia. MMA monomer obtained from Merck Schuchardt, Hohenburn Germany was used for grafting onto OPEFB fibers. Hydrogen peroxide (H_2O_2) of analytical grade produced by QR&C, Malaysia was used as an initiator whilst ammonium ferrous sulfate obtained from BDH Sigma-Aldrich Chemie GmbH, Steinheim, Germany was used as a catalyst. All solvents and other chemicals of analytical grade were used as received from manufacturers without further purification.

2.2 Removal of Inhibitor from Monomer

MMA was purified by passing the monomer through a column packed with activated alumina to remove its inhibitor (hydroquinone). Initially alumina was heated in an oven at 60°C for 24 hour to activate its content. First, reagent bottle was immersed in ice bath. Then, burette was filled with glass wool, followed by activated alumina. MMA was poured into burette through conical funnel and was allowed to flow through the burette. Purified MMA was collected in a reagent bottle and the bottle was kept in refrigerator/chiller immediately at temperature below 10°C .

2.3 Preparation of PMMA-g-Talc

Grafting copolymerization of talc and MMA was prepared by free radical polymerization under nitrogen atmosphere. One gram of talc was added to 100 ml of distilled water and dissolved in the three-necked flask. Nitrogen was purged through the talc slurry for 30 minutes. The required volume of 2.0 M initiator was injected to the flask and mixture was left for 5 minutes. The required amount of co-catalyst (ammonium ferrous sulfate) was added

to the flask and the slurry was allowed to settle for 5 minutes. Next, the required amount of MMA monomer was injected into the mixture followed by insertion of magnetic stirrer. The reaction mixture was magnetically stirred under nitrogen atmosphere at the chosen temperature and reaction period. When the reaction period was over, the reaction flask was immediately exposed to the ambience and the product was filtered. The flask was washed thoroughly with distilled water to remove product stuck on the flask and was kept in oven at 60 °C for 24 hours to constant weight.

2.5 Removal of Homopolymer

First, the initial weight of empty thimble was determined. Grafting product was taken out from the oven and allowed to cool down to room temperature. Later, this grafting product was added into thimble and the weight of thimble with grafting product (including homopolymer of PMMA) was taken. The thimble is then inserted into Soxhlet Extractor and the extraction was run for 24 hours to remove homopolymer of PMMA. Afterwards the thimble was dried in an oven at 60 °C for another 24 hours until constant weight was achieved. The thimble was removed from the oven and immediately transferred to desiccators to avoid thimble from absorbing the moisture. The thimble was allowed to cool down to room temperature. Finally, the weight of thimble and grafting product without homopolymer of PMMA was determined. The grafting percentage, % G and grafting efficiency, %E were determined by using Equations 1 and 2, respectively.

$$\text{Grafting Percentage, \% G} = \frac{w_3 - w_1}{w_1} \times 100\% \quad (1)$$

$$\text{Grafting Efficiency, \% E} = \frac{w_2 - w_1}{w_3 - w_1} \times 100\% \quad (2)$$

Given that w_1 , w_2 , w_3 is weight of original talc, weight of grafted product after copolymerization and weight of grafted product after copolymerization and purification respectively.

2.6 Fourier Transform Infrared (FTIR)

This analysis had been used to identify the related functional groups present in the talc and PMMA-g-talc filler. Infrared (IR) spectra of the filler were recorded on a Fourier Transform Infrared Spectrometer (Perkin Elmer Spectrum 2000). The presence of PMMA on the filler was indicated by additional functional groups in FTIR spectra.

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3.0 RESULTS AND DISCUSSION

3.1 Reaction Time

The effect of reaction time on the grafting parameters was conducted by varying the reaction time from 30 minutes to 90 minutes with interval time of 15 minutes. The plot of grafting level and efficiency on respective time is shown in Figure 1.

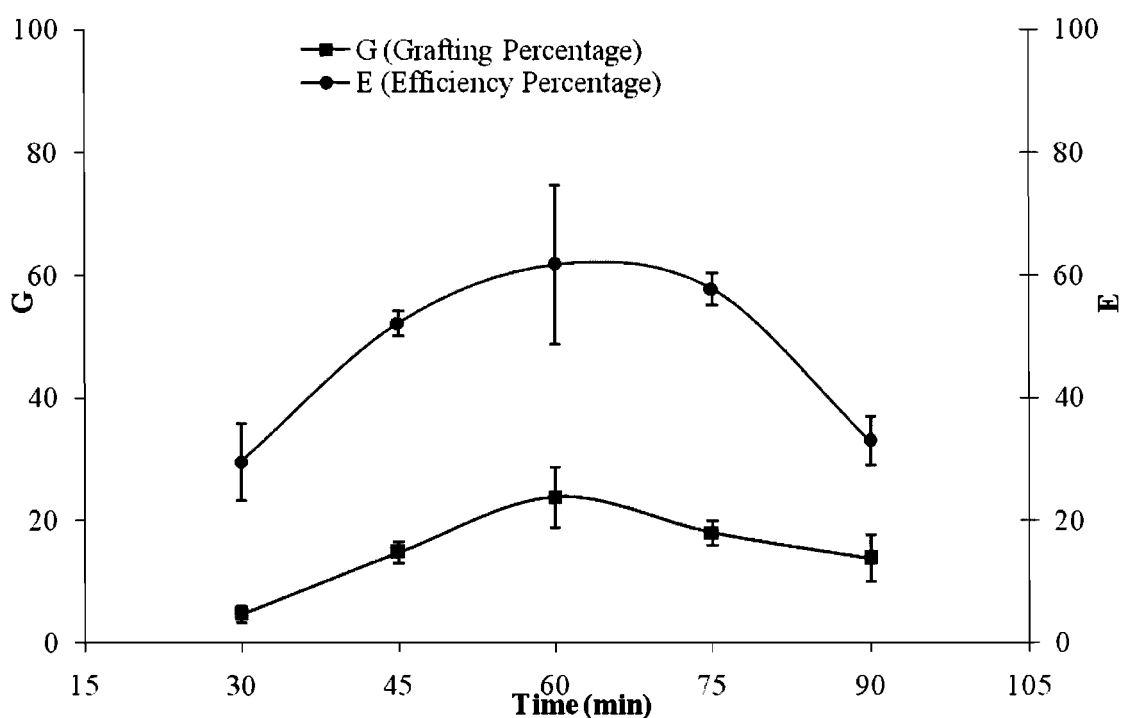


Figure 1 : Effect of reaction time on grafting parameter. Reaction temperature, 60 °C; MMA, 47.15 mmol; H₂O₂, 3.92 mmol; Fe²⁺, 0.262 mmol.

It can be seen that the grafting percentage and grafting efficiency increase at the beginning of the time reaction. This increment is continuing until it reaches 60 minutes of reaction time. The low grafting percentage at the beginning is due to the slow reaction between talc and MMA [4]. The increment in grafting parameters might due to the more availability of active species which give more graft copolymer [5]. However reduction of grafting level is noticed at elevated reaction period. This may be due to the retardation of diffusion after some polymer formed on polymer surface and deterioration of growing grafted chains with increases in time [6]. The reduction also may be due to degradation of the grafted chain on filler surface [7].

3.2 Reaction Temperature

Temperature is vital in determining the extent of grafting. In general, grafting yield increases with increases in temperature until a limiting value is reached [4]. In this study, effect of temperature on grafting was investigated between 30 °C to 70 °C with interval 10 °C each.

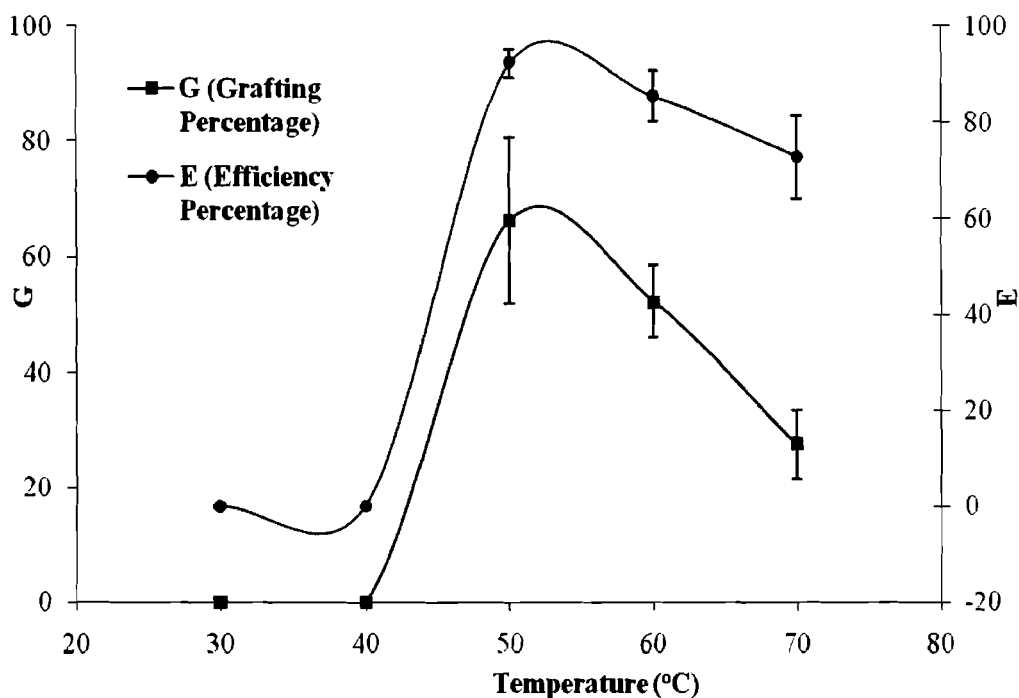


Figure 2 Effect of reaction temperature on grafting parameters. Reaction time, 60 min; MMA, 47.15 mmol; H₂O₂, 3.92 mmol; Fe²⁺, 0.262 mmol.

Figure 2 shows that the grafting reaction only occurs when the temperature is higher than 40 °C. The percent graft yield increased with increasing of temperature up to 52 °C, and beyond this temperature the graft yield decreases. This increase may be attributed to swellability of talc in the substrate and enhancement of rate of diffusion of monomer with increase of temperature. The percentage of grafting yield and efficiency at this temperature were 66.3% and 92.2%, respectively. This is because at higher temperature, decomposition of hydrogen peroxide increases, thus producing a lot of free radicals. Some of the free radicals create active centers on the filler, whereas the remaining radicals initiate the homopolymerization. The decrement in grafting percentage and efficiency at higher temperature might be due to the premature termination of growing grafted chains by excess of free radicals at higher temperature.

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3.3 Initiator Concentration

The graft copolymerization reaction was conducted by varying the concentration of H_2O_2 from 1 to 3 ml.

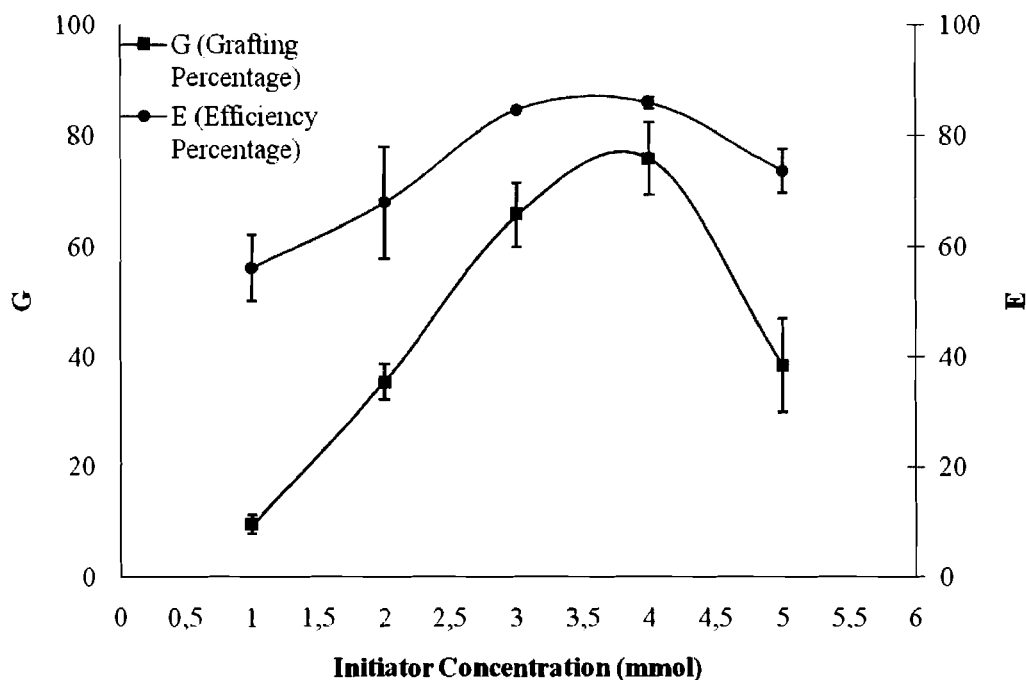


Figure 3 : Effect of initiator concentration on grafting parameters. Reaction time, 60 min; MMA, 47.15 mmol; H_2O_2 , 3.92 mmol; Fe^{2+} , 0.262 mmol.

It was observed that the grafting percentage and efficiency increase with increasing of H_2O_2 concentration from 1 ml to 2.5 ml. The increment in grafting parameters might be due to progressive reduction of H_2O_2 with ferrous ion that produces increased number of free radicals [5]. The increasing percentage of grafting also may be explained by reactions of Fe^{2+} ions with H_2O_2 which produced more hydroxyl radicals to produce macroradicals with talc [9]. The decrease in grafting parameters beyond 2.5 ml may be due to the enhanced rate of termination. When H_2O_2 is in large excess then it is decomposed to oxygen and water, since O_2 acts as scavenger of free radicals so all the grafting parameters decreased [5].

3.4 Fourier Transform Infrared

The presence of PMMA on the filler was verified by the Fourier Transform Infra Red (FTIR) spectra of talc and PMMA-g-Talc, as shown in Figure 4.

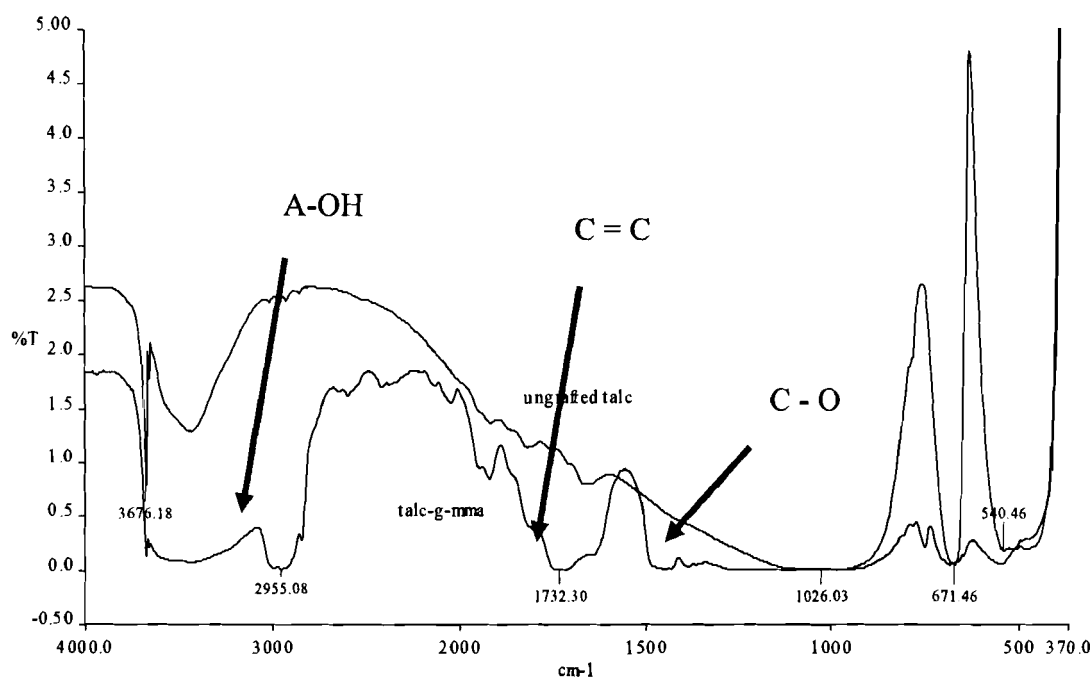


Figure 4 : FTIR spectra for talc and PMMA-g-talc

Both spectra show a characteristic broad absorption band of the hydroxyl group around $3500 - 3100 \text{ cm}^{-1}$. This is attributed to OH stretching vibrations of talc constituent of talc and moisture. Reduction of hydroxyl broad absorption band in PMMA-g-talc reveals that grafting has successfully taken place at the hydroxyl group shown in Figure 4. The presence of the peak near 1730 cm^{-1} in talc spectrum could be associated to C=O stretching of carboxylic groups in talc. The increase in intensity of C=O peak in the spectrum of PMMA-g-talc indicates that the presence of an ester group from MMA which provides strong evidence of PMMA presence. The increment of intensity at peak near 1251 cm^{-1} in the PMMA-g-talc spectra may be associated to the CO-OCH₃ stretching of PMMA. This result is a proof of presence of MMA functional group in talc.

4.0 CONCLUSION

The graft copolymerization of PMMA onto talc has been successfully carried out by free radical using hydrogen peroxide, H₂O₂ and ferrous ions as a redox initiator/co-catalyst system. The grafting level and efficiency was found to depend on reaction period, reaction temperature and monomer concentrations. The optimum conditions for reaction period, reaction temperature and monomer concentrations were 60 minutes, 52 °C and $4.9 \times 10^{-3} \text{ mol}$, respectively. Achievement of the required grafting level in the shortest time is cost effective. The maximum percentage of grafting (75.91%) was achieved when the reaction was carried out under these optimum conditions. The presence of functional group of PMMA on the talc as well as reduction in hydroxyl group in PMMA-g-talc as evidence of grafting was characterized by Fourier-transform infrared spectroscopy.

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